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⑭ Date of filing: 16.10.90

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㉒ Reactive silicone and/or fluorine containing hydrophilic prepolymers and polymers thereof.

㉓ Vinyl unsaturated copolymers are described which are obtained in a two-step process and which consist of monomeric units A, B, C, D and E, copolymerized in a first step, and in a second step reacted with a reactive vinyl monomer M_v, and in which A is a silicon or fluorine containing vinyl monomer, 20-79.5% by weight; B is N,N-dimethylacrylamide, N-vinylpyrrolidone, or N-vinylacetamide, 20-79.5% by weight; C is an active hydrogen containing vinyl monomer, 0.5-25% by weight; D are other copolymerizable comonomers, 0-30% by weight, and E is a chain transfer agent, 0-10 mol percent. M_v is a vinyl unsaturated isocyanate.

These vinyl unsaturated polymers are useful, either by themselves or in combination with other copolymerizable vinyl monomers, as heat or UV-curable coatings or glass, plastic, wood, paper, textiles, metal or ceramics, said coatings possessing low surface energies and low refractive indices. They are especially useful as UV-curable hydrophilic coatings and water-swelling biocompatible polymers, especially fully molded highly oxygen-permeable contact lenses.

EP 0 425 436 A3



EUROPEAN SEARCH
REPORT

EP 90 81 0791

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 202 (C-432)[2649], 30th June 1987; & JP-A-62 25 104 (ASAHI GLASS CO., LTD) 03-02-1987 "Abstract" -----	1	C 08 F 8/30 G 02 B 1/04		
A	EP-A-0 168 126 (SHOWA HIGHPOLYMER CO.) "Claims 1-6; pages 6,7" -----	1			
A	US-A-4 467 073 (W.S. CREASY) "Claims 1-14" -----	1			
D,A	US-A-4 650 843 (Y. YOKOHAMA) "Claims 1-5" -----	1			
D,A	US-A-4 139 692 (K. TANAKA) "Claims 1-11" -----	1			
D,A	US-A-3 928 299 (H.J. ROSENKRANZ) "Claim 1" -----	1			
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
			C 08 F		
The present search report has been drawn up for all claims					
Place of search	Date of completion of search	Examiner			
The Hague	14 May 91	PERMENTIER W.A.			
CATEGORY OF CITED DOCUMENTS					
X: particularly relevant if taken alone					
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These vinyl unsaturated polymers are useful, either by themselves or in combination with other copolymerizable vinyl monomers, as heat or UV-curable coatings or glass, plastic, wood, paper, textiles, metal or ceramics, said coatings possessing low surface energies and low refractive indices. They are especially useful as UV-curable hydrophilic coatings and water-swelling biocompatible polymers, especially fully molded highly oxygen-permeable contact lenses.

**REACTIVE SILICONE AND/OR FLUORINE CONTAINING HYDROPHILIC PREPOLYMERS AND POLYMERS
THEREOF**

Beginning with the introduction of poly-(2-hydroxyethyl methacrylate) (poly-HEMA) by Wichterle (U.S. Patent No. 3,220,960), hydrogels, that is water-insoluble, but water-swollen polymers have become ever more important as components in biomedical application, be they implants, prostheses or drug delivery devices, due to their excellent biocompatibility and permeability. Poly-HEMA based hydrogels have become 5 the major soft contact lens material due to their outstanding comfort characteristics and sufficiently high oxygen permeability ($O_2 \cdot DK$). Soft contact lenses conform very tightly to the cornea and therefore, at ~ 0.1 mm thickness, need to have an $O_2 \cdot DK$ of at least 5-6 barrers, if damage to the cornea is to be prevented during daily wear.

The $O_2 \cdot DK$ of an acrylic polymer, which does not contain either silicone or fluorine, is primarily 10 determined by its water content and rises from zero at zero % H_2O to 6.5 at ~ 39% H_2O (for poly-HEMA), 12.5 at ~ 50% H_2O to 23 at ~ 60% H_2O . However, as the water content is increased, hydrogel strength is drastically decreased and in order to maintain durability lens thickness has to be increased. This in turn counteracts the higher $O_2 \cdot DK$, because it reduces oxygen-transmissibility, $P = O_2 \cdot DK/l$ (l = lens thickness).

15 It is highly desirable to have a contact lens material, or indeed a hydrogel for biomedical applications in general, which is strong, comfortable to wear and has an inherently much higher $O_2 \cdot DK$ than conventional hydrogels. Such hydrogels can be made by incorporation of other oxygen-flux enhancing groups into the polymer, most notably siloxane groups and fluoroalkyl groups.

Both types of hydrogels have been described in the prior art. Polysiloxane-dimethacrylate as well as 20 polysiloxane-block-polyethyleneoxide dimethacrylate copolymers with water soluble vinyl monomers have been described in U.S. 4,136,250 for use in drug delivery, but also for contact lens applications; similar compositions are disclosed in U.S. 4,605,712.

Although these polymers show excellent strength and toughness, they are limited in the amount of 25 siloxane groups which can be incorporated without producing phase-separation and opacity because the siloxane is part of a rather high molecular weight polysiloxane block.

Larger amounts of siloxane groups can be built into clear hydrogels, if oligosiloxanyl-silyl alkyl (meth)-acrylates are used as comonomers; a more random distribution of siloxane groups prevents the formation of large, incompatible domains.

Such oligosiloxanyl-silyl groups containing hydrogels of prior art, which are useful as contact lens 30 materials are disclosed in U.S. 4,139,692 and U.S. 4,139,513, specifying tri-siloxy alkylmethacrylate, with the OH-group required for compatibility.

U.S. 4,182,822 and U.S. 4,343,927 describe N-vinyl pyrrolidone and C₁-C₄-dialkyl acrylamide-copolymers with oligosiloxanyl alkylene-methacrylates.

The following patents describe prior art compositions consisting of fluorinated hydrogels. U.S. 35 4,433,111, and U.S. 4,493,910 describe hydrogels and contact lenses obtained by copolymerization of 20-40 mol % substituted or unsubstituted acrylamide or methacrylamide; 25-55 mol % N-vinylpyrrolidone (NVP); 5-10 mol % hydroxy-alkyl(meth)acrylate; 1-10 mol % (meth)-acrylic acid, and 1-9 mol % of a perfluoroalkyl-alkylene (meth)acrylate; the perfluoroalkyl groups act to reduce protein deposition.

U.S. 4,640,965 describes hydrogels and contact lenses obtained by copolymerization of hydroxy-40 fluorooalkyl styrene (5-60%, by weight) with hydroxyalkyl (meth)acrylates or N-vinylpyrrolidone (40-95%, by weight); the hydroxy group is necessary to attain the required compatibility.

U.S. 4,638,040 describes the synthesis of 1,3-bis(trifluoroacetoxy) propyl-2-methacrylate polymers and their use as hydrogel-contact lens materials and ocular implants after hydrolysis.

U.S. 4,650,843 describes hydrogel contact lens materials consisting essentially of copolymers of 59-45 95% (by weight) of 2-hydroxyethyl methacrylate and 5-35% (by weight) of fluorinated methacrylates with up to 5 F-atoms.

In most cases the range of clear compositions is very limited; the commercially available fluorinated (meth)acrylates can be incorporated in only relatively small amounts; alternatively, complicated, hydroxylated F-monomers have to specially be synthesized to achieve better solubility in NVP or HEMA (U.S. 50 4,640,965).

In U.S. patent No. 4,954,587 we have described unique, highly oxygen permeable fluorinated hydrogels which are copolymers of perfluoroalkyl substituted (meth)acrylates and N,N-dimethyl-acrylamide.

In all the prior art examples, low molecular weight monomers serve as starting materials for the polymerization. While this is convenient for doing bulk-polymerizations in a closed mold, it is less practical

for curing of films or surface coatings, for example by UV-irradiation; then large amounts of monomers can evaporate, posing health hazards and irreproducibly altering the composition of the coating. Also, because of the high concentration of reactive double bonds during bulk polymerization, and the exothermic nature of the reaction, temperature is often difficult to control and shrinkage can occur in the mold as well. On the other hand, if solution polymerizations are carried out, as is sometimes desirable when otherwise incompatible comonomers have to be combined, long polymerization times are required to achieve high conversions of monomers.

It has now been discovered that linear, water soluble copolymers with a high siloxane and/or fluorine content and pendent vinyl unsaturated groups can be prepared in high yield, which are ideally suited to make by UV-curing water swellable and oxygen permeable coatings and films or shaped articles, like contact lenses. These linear unsaturated copolymers, hereinafter called prepolymers, are made in a two-step process by:

- (1) copolymerization, in bulk or in solution of (A) 20 to 79.5% by weight of a silicon or fluorine containing vinyl monomer or mixture thereof, such as oligosiloxanylsilyl-alkyl methacrylates or perfluoroalkyl substituted alkyl acrylates or methacrylates, as oxygen flux enhancing comonomers; (B) 79.5 to 20% by weight of N,N-dimethylacrylamide, N-vinylpyrrolidone or N-vinylacetamide or mixtures thereof, such as a comonomer mixture consisting of a N,N-dimethylacrylamide or N-vinylpyrrolidone as main hydrophilic comonomers; (C) 0.5 to 25% by weight of an active hydrogen atom containing vinyl comonomer or mixtures thereof, such as primary or secondary-amino alkyl- or hydroxy alkyl vinyl compounds; (D) optionally up to 30% by weight of a copolymerizable ethylenically unsaturated monomer other than a monomer of component (A), (B) or (C), or mixture thereof; and (E) also optionally, up to 10 mol %, based on the total moles of components (A) to (E), of a chain transfer agent; followed by:
- (2) reaction with 0.2 to 10 mol %, based on the total moles of components (A) to (E), of an isocyanato substituted ethylenically unsaturated monomer (M_1), (or 0.1 to 10 mol %, based on C_2 -mer units of the prepolymer chain).

Vinyl unsaturated prepolymers, obtained by reaction of an active hydrogen containing prepolymer with a vinyl unsaturated isocyanate, which do however not contain silicone or fluorine, have been described in the literature; for example in U.S. 3,928,299, which discloses very broadly an unsaturated polymer of over 1000 MW; neither silicone, fluorine or hydrogels are mentioned or disclosed; in U.S. 4,548,983, which describes hydrogels based on alkylene glycol mono-(meth)acrylates, not N,N-dimethylacrylamide or N-vinylpyrrolidone, and which are made as shaped hydrogel articles by solution polymerization in a mold, also without fluorine or silicone.

U.S. 4,383,091 discloses the reaction product of poly-hydroxy substituted polyglycidyl ether with 2-isocyanatoethyl methacrylate.

Vinyl unsaturated prepolymers obtained by reaction of a 2-isocyanatoethyl methacrylate copolymer with, for example, 2-hydroxyethyl methacrylate, are described in U.S. 4,343,919.

No unsaturated, linear, water soluble or, after a final crosslinking step, highly water swellable copolymers have been described, which are at the same time high in fluorine or silicone content.

It is an object of this invention to provide an easily polymerizable fluorine and/or silicone containing hydrophilic prepolymer; it is a further object of this invention to provide a highly water swellable, fluorine and/or silicone containing crosslinked polymer with high oxygen permeability, which is obtained by free radical polymerization of the hydrophilic prepolymer either by itself or in combination with up to 50% by weight of other copolymerizable vinyl monomers, M_2 .

The instant invention pertains to a hydrophilic prepolymer containing silicon or fluorine or both silicon and fluorine as well as ethylenically unsaturated groups, which is the reaction product of the random copolymer of, the weight percent amounts of components (A), (B), (C), (D) and (E) being based on the total amount of said components,

- (A) 20 to 79.5% by weight of a silicon or fluorine containing vinyl monomer or mixtures thereof,
 - (B) 79.5 to 20% by weight of N,N-dimethylacrylamide, N-vinylpyrrolidone or N-vinylacetamide or mixtures thereof,
 - (C) 0.5-25% by weight of a vinyl monomer containing an active hydrogen atom or mixtures thereof,
 - (D) 0 to 30% by weight of an ethylenically unsaturated monomer or mixtures thereof other than a monomer of component (A), (B) or (C),
 - (E) 0 to 10 mol %, based on the total moles of components (A), (B), (C), (D) and (E) of a chain transfer agent, with
- (M_1) 0.2 to 10 mol %, based on the total moles of components (A), (B), (C), (D) and (E), of an ethylenically unsaturated isocyanate.

The prepolymer is synthesized in a two-step process, either in bulk or in solution, by free radical

initiated copolymerization of (A), (B), (C), (D) and (E) followed by reaction with (M_v).

The above-described prepolymer, containing ethylenically unsaturated groups, can be cured to a crosslinked homopolymerization product when the prepolymer is subjected to free radical polymerization induced by heat or UV irradiation.

Said prepolymer can also be cured to a crosslinked copolymerization product when the prepolymer is polymerized in combination with other vinyl monomers (M-2), such as those described for components (A), (B) and (D) for the prepolymers.

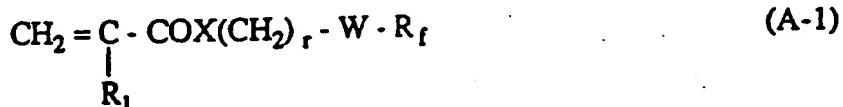
Preferably the crosslinked product is the homopolymerization product of the prepolymer; or is the copolymerization product of (a) 95 to 70% by weight of prepolymer, and (b) 5 to 30% by weight of comonomer (M-2); most preferably, the copolymerization product of (a) 90 to 75% by weight of prepolymer, and (b) 10 to 25% by weight of comonomer (M-2).

These crosslinked products are useful as coatings, films or shaped articles, particularly in biomedical devices and especially in contact lenses.

15

Monomer A:

The fluorinated and/or silicon containing monomers (A) useful for making the novel polymers of this invention are acrylic or styrenic monomers. Fluorine-containing monomers (A-1) are vinyl monomers containing at least three fluorine atoms selected from the group consisting of hexafluoroisopropyl acrylate or methacrylate, perfluorocyclohexyl acrylate or methacrylate, 2,3,4,5,6-pentafluorostyrene or the acrylate or methacrylate esters or amides of the formula



25

wherein

30 R_f is $-(\text{CF}_2)_n\text{CF}_2\text{L}$ or $-(\text{CF}_2\text{CF}_2)_q\text{OCF}(\text{CF}_3)_2$.

R^1 is hydrogen or methyl,

X is oxygen or $-\text{NR}_7-$ wherein R_7 is hydrogen or an alkyl group with 1-5 carbon atoms,

r is an integer from 1-4,

t is an integer from 0-14,

35 q is an integer from 1-3,

L is hydrogen or fluorine, with the proviso that, when t is 0, L is fluorine, and

W is a direct bond or a divalent group of the structure $-\text{NR}_7-\text{CO}-$; $-\text{NR}_7\text{SO}_2-(\text{CH}_2)r-$; $-\text{NR}_7\text{SO}_2-$; $-\text{S}-(\text{CH}_2)_r-$; $-\text{NH}(\text{CH}_2)_r-\text{NR}_7-(\text{CH}_2)_r-\text{NR}_7\text{SO}_2-$; $-\text{NH}(\text{CH}_2)_r\text{NR}_7\text{SO}_2-\text{CH}_2-$ or $-\text{CF}(\text{CF}_3)(\text{OC}_3\text{F}_8)_q-\text{O}-$.

Typical examples are 1,1,2,2-tetrahydroperfluorodecyl acrylate and methacrylate, 1,1,2,2-tetrahydroperfluoroctyl acrylate and methacrylate and N-(1,1,2-tetrahydroperfluoroctyl)-methacrylamide or acrylamide, and heptafluoropropyl-methyl methacrylate.

Other useful fluorinated monomers include hexafluoroisopropyl acrylate, hexafluoroisopropyl methacrylate, perfluorocyclohexyl methacrylate, and 2,3,4,5,6-pentafluoro styrene; the acrylates and methacrylates of fluoroalkyl substituted amido-alcohols, such as of $\text{C}_7\text{F}_{15}\text{CON}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{OH}$; of sulfonamido-alcohols, such as of $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)\text{C}_2\text{H}_4\text{OH}$ and $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{C}_2\text{H}_4\text{OH}$; of perfluoroether alcohols, such as of $\text{C}_3\text{F}_7-\text{O}(\text{C}_3\text{F}_6\text{O})_2\text{CF}(\text{CF}_3)-\text{CH}_2\text{OH}$ or $(\text{CF}_3)_2\text{CFO}(\text{CF}_2\text{CF}_2)_2-\text{CH}_2\text{CH}_2\text{OH}$; and the acrylates and methacrylates of fluorinated thioether alcohols of structure $\text{CF}_3(\text{CF}_2)_r\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{OH}$; acrylates and methacrylates of sulfonamido-amines, such as of $\text{R}_1\text{SO}_2\text{N}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{NH}_2$ and $\text{R}_1\text{CH}_2\text{SO}_2\text{NH}(\text{CH}_2)_2\text{NH}_2$; of amido-amines, such as of $\text{R}_1\text{CONH}(\text{CH}_2)_2\text{NH}_2$; as well as the vinyl monomers obtained by reaction of these aforementioned fluorinated alcohols and amines with 2-isocyanatoethyl acrylate or methacrylate or m-isopropenyl- α,α -dimethylbenzyl isocyanate.

Preferred are fluorinated monomers of formula (A-1) in which X is oxygen, W is a direct bond, and R_f is $(\text{CF}_2)_n\text{CF}_2\text{L}$ wherein t is an integer from 0 to 11.

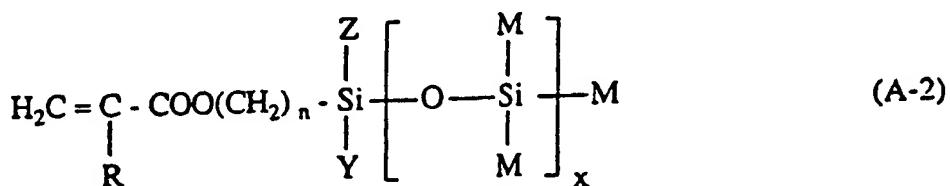
Further preferred are fluorinated monomers in which X is oxygen, W is a direct bond, r is 1 or 2, t is 1

55 to 10 and L is fluorine.

Preferred are hexafluoroisopropyl methacrylate, trifluoroethyl methacrylate, and 1,1,2,2-tetrahydroperfluoroctyl and 1,1,2,2-tetrahydroperfluorodecyl acrylate and methacrylate, with 1,1,2,2-tetrahydroperfluoroctyl acrylate being most preferred.

Useful silicon containing monomers, A-2, are acrylates and methacrylates of siloxy group substituted alkanols with at least 2-10 silicon atoms, for instance oligosiloxanyl-alkyl esters of formula:

5



10

wherein Z and Y are methyl, phenyl or Q where Q is

15



20

wherein

M is methyl or phenyl,

n is 2 to 4,

x is 0 to 6, with the proviso, that if x = 0, at least one of Z or Y is Q, and

25 R is hydrogen or methyl.

Also useful are the corresponding mono- or diitaconates.

Typical representatives include: tris(trimethylsiloxy-silyl)propyl (meth)-acrylate, triphenyldimethyl disiloxanylmethyl (meth)acrylate, pentamethyl-disiloxanymethyl (meth)acrylate, tert-butyl-tetramethyl-disiloxanymethyl(meth)acrylate, methyl-di(trimethylsiloxy)silylpropylglyceryl (meth)acrylate; pentamethyldisiloxanyl-methyl methacrylate; heptamethyl-cyclotetrasiloxoymethyl methacrylate; heptamethyl-cyclotetrasiloxo-propyl methacrylate; (trimethylsilyl)-decamethyl-pentasiloxy-propyl methacrylate; dodecamethyl-pentasiloxypropyl methacrylate.

The preferred comonomer A-2 is tris-(trimethylsiloxy-silyl)-propyl methacrylate.

35

Monomer B:

Useful monomers B are aprotic, water soluble monomers, like N,N-dimethylacrylamide, N-vinylpyrrolidone and N-vinyl acetamide. Preferred monomer B is N,N-dimethylacrylamide.

40

Monomer C:

45 Useful are hydroxy and amino-substituted vinyl monomers, among them:
2-hydroxyethyl-, 2-or 3-hydroxypropyl-, 4-hydroxybutyl acrylate and methacrylate; glycerol methacrylate; N-2-hydroxyethyl- and N-3-hydroxypropyl methacrylamide; 2-hydroxyethyl and 4-hydroxybutyl vinyl ether; bis-hydroxyethyl maleate and fumarate; N-tert-butyl-aminoethyl methacrylate, and aminostyrene; also acrylic and methacrylic acid and di-, tri-, tetra- and polyethylene glycol acrylates and methacrylates.

50

Preferred monomers C are 2-hydroxyethyl methacrylate and N-tert-butyl aminoethyl methacrylate.

Monomer D:

55 The monomers (D) which can be present in the polymers of this invention can be any other copolymerizable vinyl monomer, like an ester or amide of acrylic or methacrylic acid with from 1-20 carbon atoms in a linear or branched aliphatic, e.g. alkyl, cycloaliphatic or aromatic group containing ester or amide group, and which may be interrupted by hetero atoms like sulfur or oxygen; analogous mono- or di-esters of

maleic and itaconic acid; alkyl vinyl ethers with 1 to 10 carbon atoms in the alkyl group, vinyl esters of C₁ to C₁₂-carboxylic acids, styrene and alkyl substituted styrene and α -methylstyrene; N-alkyl-acrylamides and methacrylamides, N-alkyl and N,N-dialkylamino-alkyl methacrylates and methacrylamides.

- 5 Representative examples include: methyl acrylate, ethyl acrylate, n- and iso-propyl acrylate, cyclohexyl acrylate, trimethyl-cyclohexyl acrylate, phenyl acrylate, benzyl acrylate, octyl acrylate, 2-ethylhexyl acrylate and all the corresponding methacrylates, furfuryl acrylate and methacrylate; methoxy-ethyl-, ethoxy-ethyl-, butoxy-ethyl- and ethoxy-ethoxy ethyl acrylate and methacrylate; glycidyl methacrylate; N-isopropylacrylamide; dimethylamino-ethyl methacrylate and methacrylamide.

10

Chain Transfer Agent E:

Many compounds can act as chain transfer agents, as known to those skilled in the art of free-radical initiated polymerization, and include, most typically, halogenated molecules and thiols.

15

Especially useful chain transfer agents E are thiols like: alkyl thiols, where alkyl is a linear or branched hydrocarbon residue with 3-21 carbon atoms; thio-glycerol; mercaptoethanol; mercaptoacetic acid; mercapto-propionic acid, mercaptomaleic acid; cysteine; mercapto-N,N-dimethyl-aminoethylene. Also useful are fluorinated thiols like C₃-C₁₄F₇-29-ethyl mercaptans.

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Preferred are C₅-C₁₄-alkyl mercaptans and C₄-C₁₂-perfluoroalkyl ethyl mercaptans and especially C₆F₁₃CH₂CH₂SH.

Monomer M_v:

- 25 Vinyl unsaturated isocyanates useful to react with the reactive prepolymer [A-B-C-D-E] are 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, and 1,1-dimethyl-2-isocyanatoethyl acrylate.

Such compounds and their preparation are disclosed, for example, in U.S. Patent No. 2,718,516 and British Patent No. 1,252,099.

- 30 Other useful isocyanates include isocyanatoalkyl vinyl ethers, such as 2-isocyanatobutyl vinyl ether, and styrene isocyanate and m-isopropenyl- α,α -dimethylbenzyl isocyanate. Also useful are isocyanates obtained by the reaction of one mole of a hydroxy- or aminoalkyl acrylate or methacrylate with one mole of a diisocyanate of structure R₃(NCO)₂.

- 35 R₃ is a divalent radical derived from an aliphatic, cycloaliphatic or aromatic diisocyanate. Examples of such useful acrylates and methacrylates include 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl methacrylate, or t-butylaminoethyl methacrylate; suitable diisocyanates include isophorone diisocyanate, (3,3,4)-trimethylhexane-1,6-diisocyanate, toluene diisocyanate, diphenylmethane-4,4'-diisocyanate and the like.

Most preferred are 2-isocyanatoethyl methacrylate and m-isopropenyl- α,α -dimethylbenzyl isocyanate.

- 40 The compounds A, B, C, D, E and M_v are present in the prepolymers of this invention in amounts where
 (A) is 30-69.5% by weight;
 (B) is 69.5 to 30% by weight;
 (C) is 0.5 to 25% by weight;
 (D) is 0 to 30% by weight;
 45 (E) is 0 to 10 mol % (of monomers);
 (M_v) is 0.2 to 10 mol % (of monomers).

Preferred are prepolymers, where

- 50 (A) is 30 to 69%,
 (B) is 69 to 30%,
 (C) is 1 to 20%,
 (D) is 0 to 25%,
 (E) is 0 to 5 mol %, and
 (M_v) is 0.5 to 6 mol %.

Most preferred are prepolymers, where

- 55 (A) is 40 to 55%,
 (B) is 55 to 40%;
 (C) is 5 to 15%,
 (D) is 0 to 15%.

(E) is 0 to 2 mol %, and

(M_v) is 1 to 5 mol %.

It has further been discovered, that fluorine and/or silicone containing reactive prepolymers, which are not hydrophilic can be made by the same 2-step process. Such reactive prepolymers are thus another object of this invention, consisting of

- (A) 20-79.5% by weight of a silicon or fluorine containing vinyl monomer or mixture thereof,
- (C) 0.5-25% by weight of a vinyl monomer containing an active hydrogen atom, or mixtures thereof,
- (D) 20-79.5% by weight of an ethylenically unsaturated monomer or mixtures thereof, other than monomers of component (A) or (C),
- (E) 0 to 10 mol %, based on the total moles of components (A), (C), (D) and (E) of a chain transfer agent, and
- (M_v) 0.2-10 mol %, based on the total moles of components (A), (C), (D) and (E) of an ethylenically unsaturated isocyanate.

Such fluorine or silicon containing reactive prepolymers are useful, either by themselves or in combination with other copolymerizable monomers (M-2) as heat or a UV-curable protective coatings or films.

The fluorine and/or silicon containing prepolymers can be used either by themselves as UV-curable components, or they can preferably be copolymerized with 5 to 60% by weight of one or more copolymerizable vinyl monomer, M-2.

Useful comonomers M-2 are the ones already described as prepolymer components A, B, C and D and may be either the same or different from the ones used for the prepolymer synthesis.

Included among the useful monomers are: methyl-; ethyl-; propyl-; isopropyl-; butyl-; isobutyl-; tert-butyl-; 2-ethoxyethyl-; 2-methoxyethyl-; benzyl-; 4-t-butylphenyl-; cyclohexyl-; trimethylcyclohexyl-; isobornyl-; dicyclopentadienyl-; norbornylmethyl-; cyclododecyl-; 1,1,3,3-tetramethylbutyl-; n-butyl-; n-octyl-; 2-ethylhexyl-; decyl-; dodecyl-; tridecyl-; octadecyl-; glycidyl-; ethylthioethyl-; furfuryl-; 2-butoxyethyl, 2-(2-ethoxyethoxy)-ethyl; hexafluoroisopropyl-; 1,1,2,2-tetrahydroperfluorododecyl-; tri-, tetra- or penta-siloxanyl propyl acrylates and methacrylates, as well as the corresponding amides; N-(1,1-dimethyl-3-oxobutyl)-acrylamide; mono- and dimethyl fumarate, maleate and itaconate; diethyl fumarate; isopropyl and diisopropyl fumarate and itaconate; mono-and diphenyl and methylphenyl fumarate and itaconate; methyl vinyl ether and methoxyethyl vinyl ether; vinyl acetate; vinyl propionate, vinyl benzoate; acrylonitrile, styrene, α -methylstyrene and tert-butylstyrene, 2-hydroxyethyl-, 2- and 3-hydroxypropyl-, 2,3-dihydroxypropyl-, polyethoxyethyl-, and polyethoxypropyl acrylates and methacrylates as well as the corresponding acrylamides and methacrylamides, sucrose-, mannose-, glucose-, sorbitol acrylates and methacrylates; and di-(2,2-hydroxyethyl) maleate; acrylamide and methacrylamide, N-methylacrylamide and methacrylamide, bisacetoneacrylamide, methylolacrylamide and methacrylamide; vinylformamide and vinylacetamide, N,N-dimethyl- and N,N-diethyl-aminoethyl acrylate and methacrylate as well as the corresponding acrylamides and methacrylamides, N-tert-butylaminoethyl methacrylate and methacrylamide, 2- and 4-vinylpyridine, 4- and 2-methyl-5-vinylpyridine, N-methyl-4-vinyl piperidine, 1-vinyl- and 2-methyl-1-vinylimidazole, para- and orthoaminostyrene, dimethylaminoethyl vinyl ether, N-vinylpyrrolidone, and 2-pyrrolidinoethyl methacrylate; acrylic and methacrylic acid, itaconic-, cinnamic-, crotonic-, fumaric- and maleic acids and lower hydroxyalkyl mono- and diesters thereof, such as 2-hydroxyethyl- and di(2-hydroxyethyl) fumarate, -maleate and -itaconate, and 3-hydroxypropyl-butyl fumarate, and di(polyalkoxy)-alkyl fumarates, maleates and itaconates; maleic-anhydride, sodium acrylate and methacrylate, 2-methacryloyloxyethylsulfonic acid, 2-acrylamido-2-methyl-propanesulfonic acid, 2-phosphatoethyl methacrylate, vinylsulfonic acid, sodium vinylsulfonate, p-styrenesulfonic acid, sodium p-styrenesulfonate, and allylsulfonic acid.

Also included are the quaternized derivatives of cationic monomers obtained by quaternization with selected alkylating agents like halogenated hydrocarbons such as methyl iodide, benzyl chloride or hexadecyl chloride; epoxides like glycidol, epichlorohydrin, ethylene oxide; acrylic acid, dimethyl sulfate; methyl sulfate, and propane sulfone.

In addition to the mono-vinyl compounds described above, M-2 can include di- and polyvinyl monomers like:

Allyl acrylate and methacrylate, ethylene glycol-, diethylene glycol-, triethylene glycol-, tetraethylene glycol-, and generally polyethylene oxide glycol diacrylates and dimethacrylates; 1,4-butanediol and poly-n-butylene oxide glycol diacrylates and dimethacrylates; propylene glycol and polypropylene oxide glycol diacrylates and dimethacrylates; thiocidiethylene glycol diacrylate and dimethacrylate; neopentylene glycol diacrylate and dimethacrylate; trimethylolpropane di- and triacrylate; pentaerythritol tri- and tetraacrylate; divinylbenzene; divinyl ether; divinyl sulfone; disiloxanyl-bis-3-hydroxy propyl diacrylate or dimethacrylate;

bisphenol A diacrylate or dimethacrylate; ethoxylated bisphenol A diacrylate or dimethacrylate; methylene bisacrylamide or methacrylamide, dimethylene bisacrylamide or methacrylamide; N,N'-dihydroxyethylene bisacrylamide or methacrylamide; hexamethylene bisacrylamide or methacrylamide; decamethylene bisacrylamide or methacrylamide; allyl- and diallyl maleate, triallyl melamine, diallyl itaconate, diallyl phthalate, triallyl phosphite, polyallyl sucrose, sucrose diacrylate, glucose dimethacrylate; also, unsaturated polyesters, such as poly(alkylene-glycol maleates) and poly(alkylene-glycol fumarates), like poly(propylene glycol maleate) and poly(polyalkyleneoxide glycol maleate) and polyalkyleneoxideglycol-dimethacrylates.

Preferably, the copolymerizable comonomers M-2 are present in amounts of 5-30% by weight, most preferably 10-25% by weight.

10

Synthesis

The reactive silicone and fluorine containing prepolymers of this invention are synthesized in a 2-step process via conventional free-radical polymerization, as known to those skilled in the art; in a first step, monomers A, B, C, D and chain transfer agent E are mixed together with a free-radical generating initiator and co-polymerized, either in bulk or in solution. Many thermally decomposing initiators can be used for thermal polymerization, such as peroxides and azo compounds; having half-life at the polymerization temperature of at least 20 minutes. Typical useful peroxy compounds include isopropyl percarbonate, tert-butyl peroctoate, benzoyl peroxide, lauryl peroxide, decanoyl peroxide, acetyl peroxide, succinic acid peroxide, methyl ethyl ketone peroxide, tert-butyl peroxyacetate, propionyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butyl peroxyvalate, pelargonyl peroxide, 2,5-dimethyl-2,5-bis-(2-ethylhexanoylperoxy)-hexane, p-chlorobenzoyl peroxide, tert-butylperoxybutyrate, tert-butyl peroxymaleic acid, tert-butylperoxyisopropyl carbonate, bi(1-hydroxycyclohexyl) peroxide; azo compounds include 2,2'-azo-bisisobutyronitrile; 2,2'-azo-bis(2,4-dimethylvaleronitrile); 1,1'-bis(cyclohexane carbonitrile); and 2,2'-azo-bis(2,4-dimethyl-4-methoxy-valeronitrile).

For UV initiated polymerization, photoinitiator such as diethoxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, phenothiazine, diisopropylxanthogen disulfide, benzoin and benzoin derivatives can be used.

The amount of initiator can vary from 0.002 to 4% by weight of monomers or monomer solution and is advantageously added incrementally to the reaction vessel or continuously. Preferably the reaction is carried out in an aprotic solvent. Useful solvents are ethers, like diethyl ether, ethyleneglycol-dimethyl ether; diethylene glycol-dimethyl ether; esters like ethyl acetate or isopropyl acetate; ketones like acetone, methyl ethyl ketone, methyl isopropyl ketone or methyl isobutyl ketone; lactams and lactones like N-methylpyrrolidone and γ -butyrolactone; dimethyl sulfoxide; amides, like N,N-dimethylformamide and N,N-dimethylacetamide; chlorinated solvents, like 1,1,1-trichloroethane or chloroform; aromatic solvents like toluene or benzene.

If the polymer is prepared in bulk, in order to carry out step 2 of the synthesis, it has to be dissolved in one of the aprotic solvents or in an aprotic comonomer, which may be the same or different from A, B or D and functions as component M-2. The concentration of step-1 polymer in the solvent or aprotic monomer should be low enough to result in an easily stirrable solution.

For step two of the synthesis, the required amount of M_v is added to the step-2 prepolymer solution. If the second step consists of a urethane bond formation, an amino- or metal catalyst is preferably used, like triethylamine, pyridine or dibutyltin dilaurate or stannous octoate. The reaction temperature can vary from room temperature to about 80 °C. If an urea bond is formed during the second step, no catalyst is required. The step-2 reaction is carried out until no NCO-groups are detectable by IR-analysis.

The final polymerization step is preferably carried out by UV-initiated polymerization using photoinitiators. Such initiators are well known and have been described, for example, in polymerization art, e.g., Chapter II of "Photochemistry" by Calvert and Pitts, John Wiley & Sons (1966). The preferred initiators are photoinitiators which facilitate polymerization when the composition is irradiated. Representative examples of such initiators include acyloin and derivatives thereof, such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether and α -methylbenzoin; diketones such as benzil and diacetyl, etc.; ketones such as acetophenone, α,α,α -tribromoacetophenone, α,α -diethoxyacetophenone (DEAP), 2-hydroxy-2-methyl-1-phenyl-1-propanone, o-nitro- α,α,α -tribromoacetophenone, benzophenone and p,p'-tetramethyldiaminobenzophenone; α -acryloxime esters such as benzil-(O-ethoxycarbonyl)- α -monoxime; ketone/amine combinations such as benzophenone/N-methyldiethanolamine, benzophenone/tributylamine and benzophenone/Michler's ketone; and benzilketals such as benzildimethylketal, benzildiethylketal and 2,5-dichlorobenzildimethylketal. Normally, the photoinitiator is used in amounts ranging from about 0.01 to

5% by weight of the total oligomeric composition.

Preferably, about 0.15 to 1.0% of photoinitiator is used in the polymerizable compositions.

Polymerization may be carried out in bulk in a conventional manner or in the presence of a solvent, as have been for instance described above, but which may also contain active hydrogen atoms.

5 Useful solvents include ketones, like acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone and cyclohexanone; alcohols like ethanol, isopropanol or ethyl cellosolve; ethers like ethylene glycol or diethyleneglycol-dimethyl ether; esters like ethyl acetate or isopropyl acetate; dimethyl sulfoxide; amides like N-methylpyrrolidone; N,N-dimethyl formamide; N,N-dimethylacetamide and the like, and water.

10 The polymerization is carried out in molds, which can consist of plastics, glass or metal and can be any shape. For making films and sheets, the molds are preferably made of glass plates and lined with MYLAR or other polymer films and held together by clamps, using a spacer of desired thickness. Contact lenses are preferably prepared in UV-permeable plastic molds.

15 Other free radical generating mechanisms can be employed, such as X-rays, electron-beams and UV-radiation. Preparation of fully molded contact lenses by UV-radiation in the presence of a photoinitiator such as diethoxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, phenothiazine, diisopropylanthogen-disulfide, benzoin and benzoin derivatives is a preferred method.

20 After polymerization is complete, the polymer is removed from the mold and any solvent present is either removed by vacuum drying or extraction with water and with water-soluble solvents, or water-solvent mixtures. Useful solvents are acetone, ethanol, methanol, isopropanol and the like. Azeotropic distillation is also a useful procedure to remove certain solvents. After the solvent is removed, the polymer is equilibrated in distilled water and its water content is determined gravimetrically. All subsequent measurements are carried out on the water-equilibrated polymers.

The polymerization can also be carried out in form of a coating on a substrate, like glass, plastic, metal, wood or the like, using conventional high-speed UV-curing technology.

25 The following examples further illustrate the usefulness of the invention.

Oxygen permeability is determined with a O₂-Permeometer-Model 201-T (Createch), using buffered saline (pH = 7) as electrolyte and is expressed in units.

$$30 \quad O_2 \cdot DK (\text{barriers}) = \frac{cm^3 (\text{STP}) cm \cdot 10^{-10}}{cm^2 \cdot cm \cdot cmHg} \text{ at a given thickness and temperature}$$

35 Physical-mechanical measurements - tensile strength, Young's Modulus and elongation, (E) - are carried out with an INSTRON testing apparatus, model 1123 on 0.6-1 mm thick sheets.

Water content is expressed as:

$$40 \quad \% H_2O = \frac{\text{weight of swollen polymer} - \text{weight of dry polymer}}{\text{weight of swollen polymer}}$$

45

Example 1

1a: Synthesis of Step-1 Prepolymer:

50 29.7 g Dimethylacrylamide (DMA), 25.3 g tris-(trimethylsiloxy-)silylpropyl methacrylate (Si₄MA) and 1.85 g (0.01 mol) N-t-butylaminoethyl methacrylate (t-BAMA) is dissolved in 114 g dry isopropyl acetate in a 3-necked reaction flask equipped with N₂-inlet tube, thermowatch, reflux coburner and stirrer. The flask is purged with dry nitrogen. 0.29 g 2,2'-Azobis-(2,4-dimethylvaleronitrile) (VAZO 52) are added and the mixture is stirred at 60 °C for 24 hours. A 33.5% solids prepolymer solution is obtained, indicating essentially complete conversion.

55 The step-1 prepolymer has a composition, in mol %, of:

DMA/Si₄MA/t-BAMA = 81.1/16.2/2.7.

1b: Synthesis of Vinyl-functional Prepolymer (Step-2):

- To 19.4 g (0.034 equivalent amine) of the step-1 prepolymer (58.4 g of a 33.2% solution) are added in a bottle 0.26 g (0.0017 equiv.) 2-isocyanatoethyl methacrylate (IEM), dissolved in 0.52 g dry methyl ethyl ketone. The mixture is stirred with a magnetic stir bar for 24 hours after which time all NCO- has disappeared, as determined by IR-analysis. The methacrylate functional prepolymer solution is stored under N₂ in a refrigerator. The prepolymer has a composition in mol % of:
 DMA/Si₄MA/t-BAMA/t-BAMA + IEM = 81.1/16.2/1.35/1.35.

10

Example 2:

- Using the procedure of Example 1, a step-1 prepolymer is prepared from 12.5 g DMA, 11.0 g Si₄MA, 1.5 g t-BAMA and using in addition 0.97 g (3 mol %) dodecyl mercaptan (DM) as chain transfer agent and 17.3 g dry methyl ethyl ketone as solvent.
 A 60.6% prepolymer solution is obtained; the step-1 prepolymer has a composition, in mol %, of:
 DMA/Si₄MA/t-BAMA/DM = 76.4/15.7/4.9/3.0.
 Subsequently, this prepolymer is reacted, as described in Example 1, with IEM to form a vinyl-substituted prepolymer with a composition, in mol %, of:
 DMA/Si₄MA/t-BAMA/DM/t-BAMA + IEM = 76.4/15.7/1.3/0.1/2.4.

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15

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Example 3:

- Using the procedure of Example 1, a step-1 prepolymer is prepared from 14.9 g DMA, 12.7 g Si₄MA and 1.95 g 2-hydroxyethyl methacrylate (HEMA) and using 29.5 g methyl ethyl ketone (MEK) as solvent.
 From the step-1 prepolymer, the vinyl substituted prepolymer is prepared, as a 50% solution in MEK, as described in Example 1b, using 0.01 g dibutyltin dilaurate (DBTL) as catalyst, and with a composition, in mol %, of:
 DMA/Si₄MA/HEMA/HEMA + IEM = 76.9/15.4/3.4/3.3.

25

30

Example 4:

- From the step-1 prepolymer of Example 3, a methacrylate terminated prepolymer is prepared as described in Example 3b, but having a composition, in mol %, of:
 DMA/Si₄MA/HEMA/HEMA + IEM = 76.9/15.4/4.9/1.4.

40

Example 5:

- Using the procedure of Example 1a, a step-1 prepolymer is prepared as a 60% solution in dry MEK, having the following composition, in mol %:
 DMA/R₁A/t-BAMA/DM = 79.1/12.9/5.0/4/3.0.

R₁A is a mixture of perfluoroalkyl-ethyl acrylates with a perfluoroalkyl chain length distribution of C₆F₁₃/C₈F₁₇/C₁₀F₂₁ in weight % ratios of 5.4/72.8/20.8; DMA, t-BAMA and DM are dimethylacrylamide, t-butylaminoethyl methacrylate and dodecyl mercaptan.

Using the procedure of Example 1b, a vinyl substituted fluorinated prepolymer is prepared as a 60% solution in MEK, having a composition, in mol %, of:

DMA/R₁A/t-BAMA/DM/t-BAMA + IEM = 79.1/12.9/2.5/3.0/2.54.

45

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Example 6:

- Using the procedure of Example 1a, a step-1 prepolymer is prepared as a 50% solution in MEK, having the following composition, in mol %:
 DMA/R₁A/HEMA = 79.7/13.0/7.3.

Using the procedure of Example 1b and 0.01 g DBTL as catalyst, a vinyl substituted fluorinated

prepolymer is prepared as a 50% solution in MEK, having a composition, in mol %, of:
 DMA/R₁A/HEMA/HEMA + IEM = 79.7/13.0/3.85/3.65.

5 Example 7:

Using the procedure described in Example 1a and 1b, a di-styryl functional prepolymer is prepared by using an equivalent amount of m-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI) instead of 2-isocyanatoethyl methacrylate (IEM). The obtained prepolymer has the composition, in mol %, of:
 10 DMA/Si₄MA/t-BAMA/t-BAMA + TMI = 81.1/16.2/1.35/1.35.

Example 8:

15 Using the procedure described in Example 5, a di-styryl functional prepolymer is prepared by using an equivalent amount of TMI instead of IEM. The obtained prepolymer has the composition, in mol %, of:
 DMA/R₁A/t-BAMA/DD/t-BAMA + TMI = 79.1/12.9/2.5/3.0/2.54.

20 Example 9:

The process of Example 6 is repeated, but using n-perfluorohexylethyl methacrylate as fluorinated comonomer.

25

Example 10:

The process of Example 6 is repeated, but using heptafluoropropylmethyl methacrylate (F₇MA) as fluorinated comonomer and using an amount of 2-isocyanatoethyl methacrylate (IEM) to give a prepolymer
 30 with a composition, in mol %, of:
 DMA/F₇MA/HEMA/HEMA + IEM = 80/12.5/5.65/1.85.

Example 11:

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The process of Example 5 is repeated, but using perfluoroctyl-ethyl methacrylate as fluorinated comonomer.

40 Example 12: Synthesis of Silicone Hydrogels

25 grams of the prepolymer solution of Example 3 are mixed together with 0.2 g benzoin methyl ether and the mixture is degassed in vacuo and sparged with nitrogen. The clear solution is poured in a mold consisting of 2 MYLAR-lined glass plates separated by a 1 mm thick silicone cord spacer and held together
 45 by clamps. The filled mold is exposed to UV-radiation from a SYLVANIA-Blacklite lamp for 10 hours; it is then taken apart and the MEK-swollen polymer sheet is released in water and extracted for 48 hours with frequent water change, followed by boiling it in the last water rinse for 1/2 hour and equilibration in distilled water. A clear, soft and wettable silicone hydrogel is obtained.

50

Example 13:

Using the procedure described in Example 12, a silicone hydrogel sheet is prepared, but using 20% by weight methyl methacrylate as a comonomer (M-2).

55

Example 14-17:

Using the procedure of Examples 12 and 13, silicone containing hydrogels are synthesized from the methacrylate-prepolymers of Examples 3 and 4; their compositions and properties are listed in the following table, together with those of Examples 12 and 13 and of poly-(2-hydroxy-ethyl methacrylate) hydrogel as control.

Ex. No.	Composition				H ₂ O %	Tensile Strength	Young's Modulus	E* %	O ₂ * DK (barriers)					
	Prepolymer		Comonomer											
	of Ex.	(%)	MMA %	F ₇ MA %										
12	3	100	-	-	42.3	5.0	9.6	174	28					
13	3	80	20	-	36.6	27.0	107	167	20					
14	4	100	-	-	45.3	2.9	3.9	300	39					
15	4	90	10	-	43.6	6.6	10.5	250	31					
16	4	80	20	-	37.4	29.0	16	306	28					
17	4	80	-	20	43.9	4.3	4.4	396	42					
	poly-HEMA				39.0	5.5	9.0	70	6.5					

* E is elongation

Examples 18-22: Synthesis and properties of fluorine containing hydrogels

As described in Examples 12 and 13, hydrogel sheets are prepared and tested, using the fluorinated prepolymers of Examples 6 and 10. Their composition and properties are listed in the following table, together with those of poly-(2-hydroxy ethyl methacrylate) hydrogel as control.

Ex. No.	Composition				H ₂ O %	Tensile Strength	Young's Modulus	E* %	O ₂ * DK (barriers)					
	Prepolymer		Comonomer											
	of Ex.	(%)	MMA %	Si ₄ MA %										
18	6	100	-	-	46.4	3.3	22.5	22	10					
19	6	90	10	-	43.5	6.8	33.0	44	15					
20	10	100	-	-	51.6	1.0	1.8	138	23					
21	10	80	20	-	42.4	25.0	14.0	188	5					
22	10	80	-	20	50.6	1.5	2.3	174	57					
	poly-HEMA				39.0	5.5	9.0	70	6.5					

* E is elongation

The following examples demonstrate the synthesis of non-hydrophilic prepolymers and coatings.

Example 23:

Using a 50 cc screw-cap bottle with a magnetic stir bar, 5 g C₆F₁₃-ethyl methacrylate, 2.4 g methyl methacrylate and 1.0 g 2-hydroxyethyl methacrylate are dissolved in 8.4 g methyl-propyl ketone; 0.02 g azo-bis-isobutyronitrile are added and dissolved and the mixture is sparged with nitrogen, the bottle is immersed in a thermostated glycol bath and the mixture is stirred at 65 °C for 18 hours; the mixture is allowed to cool to room temperature; a viscous, 50% solution of step-1 prepolymer is obtained.

To this solution are added 1.0 g 2-isocyanatoethyl methacrylate and 0.001 g dibutyltin dilaurate; the

mixture is stirred at room temperature for 10 hours, after which time no free NCO groups are detectable by IR, indicating the presence of the methacrylate-functional, fluorine containing prepolymer.

0.5 g DARACURE-1173 are dissolved in the mixture and a coating is deposited on MYLAR film and exposed to UV radiation for 2 hours. After evaporation of the solvent a hard, non-wettable and oil-repellent coating is obtained.

Example 24:

10 Using the procedure of Example 23, a copolymer of 5 g tris(trimethylsiloxy) silyl-propyl methacrylate, 2 g lauryl methacrylate and 1 g 2-hydroxyethyl methacrylate is prepared and reacted with 1 g 2-isocyanatoethyl methacrylate. After all NCO has reacted, 0.5 g DARACURE-1173 are added and after coating on MYLAR and UV-irradiation, a soft, tacky coating of the silicone containing polymer is obtained.

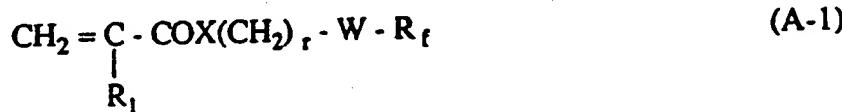
15

Example 25:

To 2 g of the DARACURE-1173 containing mixture of Example 23, is added 2 g N,N-dimethylacrylamide. The solution is filled into a MYLAR-lined glass mold of 0.5 mm thickness and irradiated by UV light for five hours. After opening the mold, a soft gel is obtained and equilibrated in water to yield a hydrogel with 55% water content.

Claims

- 25 1. A hydrophilic prepolymer containing silicon or fluorine or both silicon and fluorine as well as ethylenically unsaturated groups, which is the reaction product of the random copolymer of, the weight percent amounts of components (A), (B), (C), (D) and (E) being based on the total amount of said components,
- (A) 20 to 79.5% by weight of a silicon or fluorine containing vinyl monomer or mixtures thereof,
- 30 (B) 79.5 to 20% by weight of N,N-dimethylacrylamide, N-vinylpyrrolidone or N-vinylacetamide or mixtures thereof,
- (C) 0.5-25% by weight of a vinyl monomer containing an active hydrogen atom or mixtures thereof,
- (D) 0 to 30% by weight of an ethylenically unsaturated monomer or mixtures thereof other than a monomer of component (A), (B) or (C),
- 35 (E) 0 to 10 mol %, based on the total moles of components (A), (B), (C), (D) and (E) of a chain transfer agent, with
- (M_v) 0.2 to 10 mol %, based on the total moles of components (A), (B), (C), (D) and (E), of an ethylenically unsaturated isocyanate.
2. A prepolymer according to claim 1 wherein the fluorine containing monomer of component (A) contains at least three fluorine atoms and is selected from the group consisting of hexafluoroisopropyl acrylate or methacrylate, perfluorocyclohexyl acrylate or methacrylate, 2,3,4,5,6-pentafluorostyrene or the acrylate or methacrylate esters or amides of the formula



45

50 wherein

R₁ is -(CF₂)_tCF₂L or -(CF₂CF₂)_qOCF(CF₃)₂,

R₁ is hydrogen or methyl,

X is oxygen or -NR₇- wherein R₇ is hydrogen or an alkyl group with 1-5 carbon atoms,

r is an integer from 1-4,

t is an integer from 0-14,

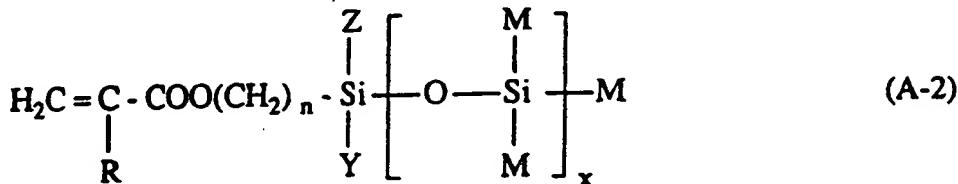
55 q is an integer from 1-3,

L is hydrogen or fluorine, with the proviso that, when t is 0, L is fluorine, and

W is a direct bond or a divalent group of the structure -NR₇-CO-; -NR₇SO₂-(CH₂)_r-; -NR₇SO₂-; -S-(CH₂)_r-; -NH(CH₂)_r-NR₇-(CH₂)_r-; -NR₇SO₂-; -NH(CH₂)_r, NR₇SO₂-CH₂- or -CF(CF₃)(OC₃F₆)_q-O-

3. A prepolymer according to claim 2 where the fluorine containing monomer is of formula A-1 where X is oxygen r is 1 or 2, W is a direct bond, t is 1 to 10 and L is fluorine.
4. A prepolymer according to claim 2 wherein the fluorine containing monomer is hexafluoroisopropyl methacrylate, 2,2,2-trifluoroethyl methacrylate, 1,1,2,2-tetrahydroperfluorooctyl- or 1,1,2,2-tetrahydroperfluorodecyl acrylate or methacrylate.
5. A prepolymer according to claim 1 wherein the silicon containing monomer A-2 of component (A) contains at least 2 to 10 silicon atoms.
6. A prepolymer according to claim 1 wherein the silicon containing monomer is of formula A-2:

10



15

wherein Z and Y are methyl, phenyl or Q where Q is

20



25

wherein

M is methyl or phenyl,

n is 2 to 4,

x is 0 to 6, with the proviso, that if x = 0, at least one of Z or Y is Q, and

R is hydrogen or methyl.

7. A prepolymer according to claim 6 wherein the silicon containing monomer A-2 is tris(trimethylsiloxy)silylpropyl methacrylate.

8. A prepolymer according to claim 1 wherein component (B) is N,N-dimethylacrylamide.

9. A prepolymer according to claim 1 wherein the vinyl monomer (C) containing an active hydrogen atom is a hydroxy or amino substituted vinyl monomer selected from the group consisting of 2-hydroxyethyl-, 2- or 3-hydroxypropyl-, 4-hydroxybutyl acrylate and methacrylate; glycerol methacrylate; N-2-hydroxyethyl- and N-3-hydroxypropyl methacrylamide; 2-hydroxyethyl and 4-hydroxybutyl vinyl ether; bis-hydroxyethyl maleate and fumarate; N-tert-butyl-aminoethyl methacrylate, and aminostyrene; also acrylic and methacrylic acid and di-, tri-, tetra- and polyethylene glycol acrylates and methacrylates.

10. A prepolymer according to claim 9 wherein the monomer (C) containing an active hydrogen atom is 2-hydroxyethyl methacrylate or N-tert-butylaminoethyl methacrylate.

11. A prepolymer according to claim 1 wherein the ethylenically unsaturated vinyl monomer of component (D) is selected from the group consisting of an ester or amide of acrylic or methacrylic acid with from 1-20 carbon atoms in a linear or branched aliphatic, e.g. alkyl, cycloaliphatic or aromatic group containing ester or amide group, and which may be interrupted by hetero atoms like sulfur or oxygen; analogous mono- or di-esters of maleic and itaconic acid; alkyl vinyl ethers with 1 to 10 carbon atoms in the alkyl group, vinyl esters of C₁ to C₁₂-carboxylic acids, styrene and alkyl substituted styrene and α-methylstyrene; N-alkyl-acrylamides and methacrylamides, N-alkyl and N,N-dialkyl amino-alkyl methacrylates and methacrylamides.

12. A prepolymer according to claim 1 wherein the chain transfer agent of component (E) is an alkyl mercaptan having 3 to 21 carbon atoms, thioglycerol, mercaptoethanol, mercaptoacetic acid, mercaptopropionic acid, mercaptomaleic acid, cysteine, mercapto-N,N-dimethylaminoethylene or a C₃₋₁₄F₇₋₂₉-ethyl mercaptan.

13. A prepolymer according to claim 12 wherein component (E) is C₅-C₁₄-alkyl mercaptan or a C₄-C₁₂-perfluoroalkylethyl mercaptan.

14. A prepolymer according to claim 1 wherein component (M_v) is 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, 1,1-

dimethyl-2-isocyanatoethyl acrylate, 2-isocyanatobutyl vinyl ether, styrene isocyanate or *m*-isopropenyl- α,α -dimethylbenzyl isocyanate or the reaction product of 2-hydroxyethyl methacrylate with toluene diisocyanate or isophorone diisocyanate in equimolar amounts.

15. A prepolymer according to claim 1 wherein the amounts of (A) to (M_v) are

- 5 (A) is 30-69.5% by weight;
- (B) is 69.5 to 30% by weight;
- (C) is 0.5 to 25% by weight;
- (D) is 0 to 30% by weight;
- (E) is 0 to 10 mol % (of monomers);
- 10 (M_v) is 0.2 to 10 mol % (of monomers).

16. A prepolymer according to claim 15 wherein the amounts of (A) to (M_v) are

- (A) is 30 to 69% by weight,
- (B) is 69 to 30% by weight,
- (C) is 1 to 20% by weight,
- 15 (D) is 0 to 25% by weight,
- (E) is 0 to 5 mol %, and
- (M_v) is 0.5 to 6 mol %.

17. A prepolymer according to claim 16 wherein the amounts of (A) to (M_v) are

- 20 (A) is 40 to 55% by weight,
- (B) is 55 to 40% by weight,
- (C) is 5 to 15% by weight,
- (D) is 0 to 15% by weight,
- (E) is 0 to 2 mol %, and
- (M_v) is 1 to 5 mol %.

25 18. A crosslinked homopolymerization product of a prepolymer according claim 1.

19. A contact lens which is the water-swollen, crosslinked homopolymerization product of a prepolymer according to claim 1.

20. A crosslinked copolymerization product of

- (a) 95 to 70% by weight of a prepolymer according to claim 1, and
- 30 (b) 5 to 30% by weight of an ethylenically unsaturated monomer (M-2).

21. A crosslinked copolymerization product of

- (a) 90 to 75% by weight of a prepolymer according to claim 1, and
- (b) 10 to 25% by weight of an ethylenically unsaturated monomer (M-2).

22. A crosslinked copolymerization product of

- 35 (a) 95 to 70% by weight of a prepolymer according to claim 2, and
- (b) 5 to 30% by weight of an ethylenically unsaturated monomer (M-2).

23. A crosslinked copolymerization product of

- (a) 95 to 70% by weight of a prepolymer according to claim 5, and
- (b) 5 to 30% by weight of an ethylenically unsaturated monomer (M-2).

40 24. A product according to claim 20 wherein the monomer (M-2) is selected from the group consisting of methyl-, ethyl-, propyl-, isopropyl-, butyl-, isobutyl-, tert-butyl-, 2-ethoxyethyl-, 2-methoxyethyl-, benzyl-, 4-t-

butylphenyl-, cyclohexyl-, trimethylcyclohexyl-, isobornyl-, dicyclopentadienyl-, norbornylmethyl-, cyclododecyl-, 1,1,3,3-tetramethylbutyl-, n-butyl-, n-octyl-, 2-ethylhexyl-, decyl-, dodecyl-, tridecyl-, octadecyl-, glycidyl-, ethylthioethyl-, furyl-, 2-butoxyethyl, 2-(2-ethoxyethoxy)-ethyl, hexafluoroisopropyl-, 1,1,2,2-tetrahydroperfluorododecyl-, 1,1,2,2-tetrahydroperfluoroctyl-, tri-, tetra- or penta-siloxanyl propyl

45 acrylates and methacrylates, as well as the corresponding amides; N-(1,1-dimethyl-3-oxobutyl)acrylamide; mono- and dimethyl fumarate, maleate and itaconate; diethyl fumarate; isopropyl and diisopropyl fumarate

and itaconate; mono- and diphenyl and methylphenyl fumarate and itaconate; methyl vinyl ether and methoxyethyl vinyl ether; vinyl acetate; vinyl propionate, vinyl benzoate; acrylonitrile, styrene, α -methyl-

50 styrene and tert-butylstyrene, 2-hydroxyethyl-, 2- and 3-hydroxypropyl-, 2,3-dihydroxypropyl-, polyethoxyethyl-, and polyethoxypropyl acrylates and methacrylates as well as the corresponding acrylamides and methacrylamides, sucrose-, mannose-, glucose-, sorbitol acrylates and methacrylates; and di-

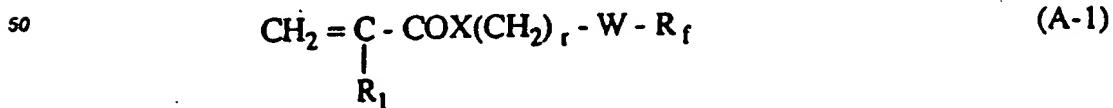
(2,2-hydroxyethyl) maleate; acrylamide and methacrylamide, N-methylacrylamide and methacrylamide, N,N-bisacetoneacrylamide, methylolacrylamide and methacrylamide; vinylformamide and vinylacetamide, N,N-

55 dimethyl- and N,N-diethyl-aminoethyl acrylate and methacrylate as well as the corresponding acrylamides and methacrylamides, N-tert-butylaminoethyl methacrylate and methacrylamide, 2-and 4-vinylpyridine, 4-

and 2-methyl-5-vinylpyridine, N-methyl-4-vinyl piperidine, 1-vinyl- and 2-methyl-1-vinylimidazole, para- and

orthoaminostyrene, dimethylaminoethyl vinyl ether, N-vinylpyrrolidone, and 2-pyrrolidinoethyl methacrylate;

- acrylic and methacrylic acid, itaconic-, cinnamic-, crotonic-, fumaric- and maleic acids and lower hydroxyalkyl mono- and diesters thereof, such as 2-hydroxyethyl- and di(2-hydroxyethyl) fumarate, -maleate and -itaconate, and 3-hydroxypropyl-butyl fumarate, and di(polyalkoxy)alkyl fumarates, maleates and itaconates; maleic-anhydride, sodium acrylate and methacrylate, 2-methacryloyloxyethylsulfonic acid, 2-acrylamido-2-methyl-propanesulfonic acid, 2-phosphatoethyl methacrylate, vinylsulfonic acid, sodium vinylsulfonate, p-styrenesulfonic acid, sodium p-styrenesulfonate, allylsulfonic acid, allyl acrylate and methacrylate, ethylene glycol-, diethylene glycol-, triethylene glycol-, tetraethylene glycol-, and generally polyethylene oxide glycol diacrylates and dimethacrylates; 1,4-butanediol and poly-n-butylene oxide glycol diacrylates and dimethacrylates; propylene glycol and polypropylene oxide glycol diacrylates and dimethacrylates; thiidiethylene glycol diacrylate and dimethacrylate; neopentylene glycol diacrylate and dimethacrylate; trimethylolpropane di- and triacrylate; pentaerythritol tri- and tetraacrylate; divinylbenzene; divinyl ether; divinyl sulfone; disiloxanyl-bis-3-hydroxy propyl diacrylate or dimethacrylate; bisphenol A diacrylate or dimethacrylate; ethoxylated bisphenol A diacrylate or dimethacrylate; methylene bisacrylamide or methacrylamide, dimethylene bisacrylamide or methacrylamide; N,N-dihydroxyethylene bisacrylamide or methacrylamide; hexamethylene bisacrylamide or methacrylamide; decamethylene bisacrylamide or methacrylamide; allyl- and diallyl maleate, triallyl melamine, diallyl itaconate, diallyl phthalate, triallyl phosphite, polyallyl sucrose, sucrose diacrylate, glucose dimethacrylate; poly-(alkylene-glycol maleates), poly(alkylene-glycol fumarates), poly(propylene glycol maleate), poly(polyalkyleneoxide glycol maleate) and polyalkyleneoxideglycol-dimethacrylates.
- 20 25. A product according to claim 22 wherein the monomer (M-2) is selected from the group methyl methacrylate, 2-methoxy-ethyl methacrylate, 2-hydroxyethyl methacrylate, tris(trimethylsiloxy silyl) propyl methacrylate, 1,1,2,2-tetrahydroperfluorooctyl- or decyl acrylate or methacrylate, hexafluoroisopropyl methacrylate and heptafluoropropyl-methyl methacrylate.
- 25 26. A product according to claim 23 wherein the monomer (M-2) is selected from the group methyl methacrylate, 2-methoxy-ethyl methacrylate, 2-hydroxyethyl methacrylate, tris(trimethylsiloxy silyl) propyl methacrylate, 1,1,2,2-tetrahydroperfluorooctyl- or decyl acrylate or methacrylate, hexafluoroisopropyl methacrylate and heptafluoropropyl-methyl methacrylate.
- 30 27. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 20.
28. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 21.
- 30 29. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 22.
- 30 30. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 23.
31. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 24.
32. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 25.
33. A contact lens which is the crosslinked, water-swollen copolymerization product according to claim 26.
- 35 34. A prepolymer containing silicone or fluorine or both silicon and fluorine as well as unsaturated groups, which is the reaction product of the random copolymer of, by weight percent based on the total amount of said components,
- (A) 20-79.5% by weight of a silicone or fluorine containing vinyl monomer or mixture thereof,
 (C) 0.5-25% by weight of a vinyl monomer containing an active hydrogen atom, or mixtures thereof,
 (D) 20-79.5% by weight of an ethylenically unsaturated monomer or mixtures thereof, other than monomers of component (A) or (C),
 (E) 0-10 mol %, based on the total moles of (A), (C), (D) and (E) of a chain transfer agent, with
 (M_w) 0.2-10 mol %, based on the total moles of components (A), (C), (D) and (E), of an ethylenically unsaturated isocyanate.
- 45 35. A prepolymer according to claim 34 wherein component (A) contains at least three fluorine atoms and is selected from the group consisting of hexafluoroisopropyl acrylate or methacrylate, perfluorocyclohexyl acrylate or methacrylate, 2,3,4,5,6-pentafluorostyrene or the acrylate or methacrylate esters or amides of the formula



55 wherein

R_1 is $-(\text{CF}_2)_q\text{CF}_2\text{L}$ or $-(\text{CF}_2\text{CF}_2)_q\text{OCF}(\text{CF}_3)_2$,

R_1 is hydrogen or methyl,

X is oxygen or $-\text{NR}_2-$ wherein R_2 is hydrogen or an alkyl group with 1-5 carbon atoms.

r is an integer from 1-4,

t is an integer from 0-14,

q is an integer from 1-3,

L is hydrogen or fluorine, with the proviso that, when t is 0, L is fluorine; and

5 W is a direct bond or a divalent group of the structure -NR₇-CO-; -NR₇SO₂-(CH₂)_r-; -NR₇SO₂-; -S-(CH₂)_r-; -NH(CH₂)_r-NR₇-(CH₂)_r-NR₇SO₂-; -NH(CH₂)_rNR₇SO₂-CH₂-or -CF(CF₃)(OC₃F₆)_q-O-

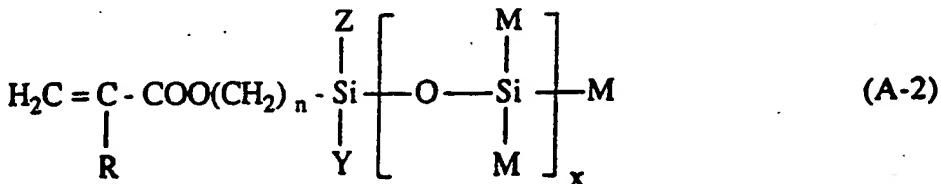
36. A prepolymer according to claim 35 where the fluorine containing monomer is of formula A-1 where X is oxygen, r is 1 or 2, W is a direct bond, t is 1 to 10 and L is fluorine.

37. A prepolymer according to claim 34 wherein the fluorine containing monomer is hexafluoroisopropyl methacrylate, 2,2,2-trifluoroethyl methacrylate, 1,1,2,2-tetrahydroperfluorooctyl or 1,1,2,2-tetrahydroperfluorodecyl acrylate or methacrylate.

38. A prepolymer according to claim 34 wherein the silicon containing monomer A-2 of component (A) contains at least 2 to 10 silicon atoms.

39. A prepolymer according to claim 34 wherein the silicon containing monomer is of formula A-2:

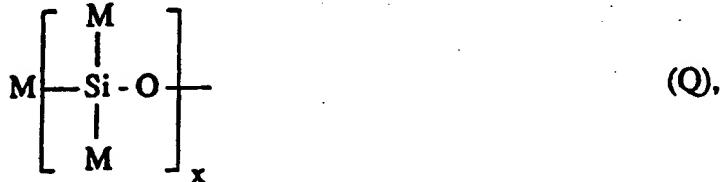
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wherein Z and Y are methyl, phenyl or Q where Q is

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wherein

35 M is methyl or phenyl,

n is 2 to 4,

x is 0 to 6, with the proviso, that if x = 0, at least one of Z or Y is Q, and

R is hydrogen or methyl.

40. A prepolymer according to claim 39 wherein the silicon containing monomer A-2 is tris(trimethylsiloxyisilyl)propyl methacrylate.

41. A prepolymer according to claim 34 wherein the vinyl monomer (C) containing an active hydrogen atom is a hydroxy or amino substituted vinyl monomer selected from the group consisting of 2-hydroxyethyl-, 2- or 3-hydroxypropyl-, 4-hydroxybutyl acrylate and methacrylate; glycerol methacrylate; N-2-hydroxyethyl- and N-3-hydroxypropyl methacrylamide; 2-hydroxyethyl and 4-hydroxybutyl vinyl ether; bis-hydroxyethyl maleate and fumarate; N-tert-butyl-aminoethyl methacrylate, and aminostyrene; also acrylic and methacrylic acid and di-, tri-, tetra- and polyethylene glycol acrylates and methacrylates.

42. A prepolymer according to claim 41 wherein the monomer (C) containing an active hydrogen atom is 2-hydroxyethyl methacrylate or tert-N-butylaminoethyl methacrylate.

43. A prepolymer according to claim 34 wherein component (M_v) is 2-isocyanatoethyl methacrylate, 2-isocyanatoethyl acrylate, 3-isocyanatopropyl methacrylate, 1-methyl-2-isocyanatoethyl methacrylate, 1,1-dimethyl-2-isocyanatoethyl acrylate, 2-isocyanatobutyl vinyl ether, styrene isocyanate or m-isopropenyl- α -dimethylbenzyl isocyanate or the reaction product of 2-hydroxyethyl methacrylate with toluene diisocyanate or isophorone diisocyanate in equimolar amounts.

44. A crosslinked homopolymerization product of a prepolymer according to claim 34.

45. A crosslinked copolymerization product of

(a) 40 to 95% by weight of a prepolymer according to claim 34, and

(b) 5 to 60% by weight of an ethylenically unsaturated monomer (M-2).

46. A process for the manufacture of a prepolymer according to claim 1 made in a two-step process

characterized by

(1) copolymerization, in bulk or in solution of (A) 20 to 79.5% by weight of a silicon or fluorine containing vinyl monomer or mixture thereof, (B) 79.5 to 20% by weight of N,N-dimethylacrylamide, N-vinylpyrrolidone or N-vinylacetamide or mixtures thereof, (C) 0.5 to 25% by weight of an active hydrogen atom containing vinyl comonomer or mixtures thereof, (D) optionally up to 30% by weight of a copolymerizable ethylenically unsaturated monomer other than a monomer of component (A), (B) or (C), or mixture thereof; and (E) also optionally, up to 10 mol %, based on the total moles of components (A) to (E), of a chain transfer agent; followed by:

(2) reaction with 0.2 to 10 mol %, based on the total moles of components (A) to (E), of an isocyanato substituted ethylenically unsaturated monomer (M_y).

47. A process for the manufacture of a crosslinked homopolymerization product according to claim 18, by conventional polymerization.

48. A process for the manufacture of a crosslinked copolymerization product according to claim 20, by conventional copolymerization.

49. Use of a prepolymer according to claim 1 for the manufacture of a contact lens.

50. Use of a copolymer according to claim 20 for the manufacture of a contact lens.

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